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THERMOPLASTIC RESIN FILM LAMINATE
[Netsusosei Jushi Firumu Sekisobutsu]

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Specification

1. Title of the invention

Thermoplastic resin film laminate

2. Patent Claim

1. A thermoplastic resin film laminate characterized by the fact that at least either plane thereof is laminated with a polyester resin composition obtained by mixing (A): A water-insoluble polyester copolymer formed from a glycol component & a mixed dicarboxylic acid component inclusive, with respect to the total dicarboxylic acid component, of 0.5 ~ 15 mol% of a metal sulfonate group-containing dicarboxylic acid at an (A)/(B) weight ratio of 100,000/5 ~ 100,000/50,000.

3. Detailed explanation of the invention

(Industrial application fields)

The present invention concerns a thermoplastic resin film laminate bearing an excellent lubricancy & flatness as well as a method for manufacturing the same.

(Prior art)

As has traditionally been known, thermoplastic resin films such as films of polyesters, polyamides, polypropylene, etc., especially polyester films and above all a polyethylene terephthalate film, bear advanced crystallinities as well as excellent transparent lusters, dynamic properties, chemical resistances, heat resistances, etc., and accordingly, they have, in recent years, come to be used for diverse purposes.

¹ Numbers in the margin indicate pagination in the foreign text.

As has been well-known in the prior art, however, in a case where the frictional coefficient of a polyester film is high, no slip can be induced between adjacent film layers, and in an extreme case, blocking becomes incurred, as a result of which not only the film handling but also film formation, above all winding, become difficult. Attempts have therefore been made in the prior art to realize the goal of lowering the film frictional coefficient by adding an inorganic or organic substance or their mixture to said film. In a case where the addition ratio of the additive(s) thus added to the film is low, however, the effects are miniscule, and in a case where the addition ratio is enlarged, the transparency, turbidity, etc. of said film rapidly deteriorate. In other words, there exists no film the frictional coefficient which has been significantly lowered at a level of transparency virtually comparable to that of its additive-free counterpart. Even in a case where $\frac{1}{2}$ an identical quantitative ratio of an identical additive is added to a polyester, furthermore, the extent of the frictional coefficient loss depends considerably on thermal treatment conditions, and this loss of magnitude becomes more conspicuous as the heat history becomes more extensive. A method for obtaining a film with an excellent lubricancy & transparency by adding a polyorganosilane, etc. to a polyester film has, on the other hand, been proposed, whereas although the lubricancy may be enhanced by enlarging the addition ratio of the polyorganosilane, the transparency loss of the film becomes unavoidable, and the dimensional stability and such mechanical properties as Young's modulus, etc. also tend to decrease, whereas although a method wherein a knurling treatment is performed prior to winding is also known, the knurled segment may become trimmed by a slit in the course of a secondary treatment, or said segment may come to exist only on either side, and thus, various problems are inherent in the manufacturing methods of the prior art.

(Problems to be solved by the invention)

The present inventors compiled intensive researches for the purpose of solving the aforementioned problems of the prior art, namely the difficulty of simultaneously conferring the flatness & lubricancy, and as a result of such efforts, the present invention has become completed.

(Mechanism for solving the problems)

In other words, the present invention concerns a thermoplastic resin film laminate characterized by the fact that at least either plane thereof is laminated with a polyester resin composition obtained by mixing (A): A water-insoluble polyester copolymer formed from a glycol component & a mixed dicarboxylic acid component inclusive, with respect to the total dicarboxylic acid component, of 0.5 ~ 15 mol% of a metal sulfonate group-containing dicarboxylic acid at an (A)/(B) weight ratio of 100,000/5 ~ 100,000/50,000. 2/3 6870

The water-insoluble polyester copolymer (A) of the present invention is a virtually water-insoluble polyester copolymer obtained by reacting a glycol component with a mixed dicarboxylic acid component comprising of 0.5 ~ 15 mol% of a metal sulfonate group-containing dicarboxylic acid and 85 ~ 99.5 mol% of a metal sulfonate group-free dicarboxylic acid. That the "polyester copolymer is virtually insoluble with water" signifies that the polyester copolymer does not dissipated into a 80°C hot water even if it is agitated within said hot water, and more specifically, the polyester copolymer weight loss is no more than 5 wt% after said polyester copolymer has been agitated within an excess of 80°C hot water over a 24-hour period.

The aforementioned metal sulfonate group-containing dicarboxylic acids are instantiated by the respective metal salts of sulfoterephthalic acid, 5-sulfoisophthalic acid, 4-sulfophthalic acid, 4-sulfonaphthalene-2,7-dicarboxylic acid, 5-(4-sulfophenoxy)isophthalic acid, etc., and of these, 5-sodiosulfoisophthalic acid & sodiosulfoterephthalic acid are especially desirable. The ratios of these metal sulfonate group-containing dicarboxylic acid components with respect to the total dicarboxylic acid component must be confined to a range of 0.5 ~ 15 mol%, for in a case where said ratio exceeds 15 mol%, the water resistance of the polyester copolymer significantly deteriorates, whereas in a case where the same is lower than 0.5 mol%, the dispersibility of a zirconium compound significantly deteriorates.

As metal sulfonate group-free dicarboxylic acids, furthermore, aromatic, aliphatic, and/or alicyclic dicarboxylic acids can be used. Aromatic dicarboxylic acids are instantiated by terephthalic acid, isophthalic acid, o-phthalic acid, 2,6-naphthalenedicarboxylic acid, etc. It is desirable for the ratios of these aromatic dicarboxylic acids respect to the total dicarboxylic acid component to be at least 40 mol%. In a case where this ratio is lower than 40 mol%, the mechanical strengths & water resistance of the polyester copolymer deteriorate. Aliphatic & alicyclic dicarboxylic acids are instantiated by succinic acid, adipic acid, sebacic acid, 1,3-cyclopentanedicarboxylic acid, 1,2-cyclohexanedicarboxylic acid, 1,3-cyclohexanedicarboxylic acid, 1,4-cyclohexanedicarboxylic acid, etc. The adhesion performances may, in some cases, be enhanced by adding these non-aromatic dicarboxylic acid components, although they generally entail mechanical strength & water resistance losses of the polyester copolymer.

The glycol component to be reacted with the aforementioned dicarboxylic acid mixture is an aliphatic glycol in possession of 2 ~ 8 carbon atoms or an alicyclic glycol in possession of 6 ~ 12 carbon atoms, whereas they are concretely instantiated by ethylene glycol, 1,2-propylene glycol, 1,3-propanediol, 1,4-butanediol, neopentyl glycol, 1,6-hexanediol, 1,2-cyclohexanedimethanol, 1,3-cyclohexanedimethanol, 1,4-cyclohexanedimethanol, p-xylylene glycol, diethylene glycol, triethylene glycol, etc. Moreover, polyethers are instantiated by polyethylene glycol, polypropylene glycol, polytetramethylene glycol, etc.

The polyester copolymer is obtained based on an ordinary melt polycondensation. In other words, it can be obtained by the direct esterification method wherein the aforementioned dicarboxylic acid component & glycol component are directly reacted & esterified by distilling & removing water and then polycondensed or the transesterification method wherein the dimethyl ester of the aforementioned dicarboxylic acid component and the glycol component are reacted & transesterified by distilling methyl alcohol and then polycondensed. Alternatively, furthermore, solution polycondensation, interfacial polycondensation, etc. are also usable, and the polyester copolymer of the present invention is not limited by polycondensation methods.

In a case where a polyester resin composition obtained by mixing the aforementioned polyester copolymer & zirconium compound is laminated on a film, a method wherein said polyester resin composition and a film precursor resin are simultaneously co-extruded from separate extrusion gates of an extruding machine, a method wherein a molten sheet of said polyester resin composition is extruded & laminated on a film, a method wherein an aqueous dispersion of a mixture of a zirconium compound & said polyester copolymer is coated on a film, etc. are conceivable, and although they are each permissible, the method wherein the aqueous dispersion of said polyester copolymer is coated is especially desirable in consideration of lubricancy, for a thin film can be formed above the base film.

On an occasion for obtaining the aqueous dispersion of said polyester copolymer, it is necessary to disperse said copolymer into water together with a water-soluble organic compound(s). Usable methods may, for example, be instantiated by a method wherein the aforementioned polyester copolymer & water-soluble organic compound are preliminarily mixed at 50 ~ 200°C, wherein water is added to the aforementioned mixture, and wherein the contents are agitated & dispersed, a method wherein said mixture is conversely added to water and wherein the contents are agitated & dispersed, and a method wherein the polyester copolymer & water-soluble organic compound are agitated at 40 ~ 120°C under the co-pervasion of water.

The aforementioned water-soluble organic compound is an organic compound yielding a solubility of at least 20 g with respect to 1 L of water at 20°C, and as such, aliphatic & alicyclic alcohol, ether, ester, and/or ketone compounds are concretely used, whereas they are instantiated by monovalent alcohols such as methanol, ethanol, isopropanol, n-butanol, etc.; glycols such as ethylene glycol, propylene glycol, etc.; glycol derivatives such as methyl Cellosolve, ethyl Cellosolve, n-butyl Cellosolve, etc.; ethers such as dioxane, tetrahydrofuran, etc.; esters such as ethyl acetate, etc.; and ketones such as methyl ethyl ketone, etc. These water-soluble organic compounds may be used either alone or as mixtures of two or more types. Of the aforementioned

compounds, butyl Cellosolve & ethyl Cellosolve are especially desirable in consideration of the water dispersibility & film coatability.

It is important for the weight-based mixing ratios of the aforementioned water-insoluble polyester polymer (A), water-soluble organic compound (C), & water (D) to satisfy $(A)/(C) = 100/20 \sim 100/5,000$ & $(C)/(D) = 100/50 \sim 100/10,000$. In a case where the ratio of the water-soluble organic compound with respect to the polyester copolymer is low and where the $(A)/(C)$ value exceeds 100/20, the dispersibility of the aqueous dispersion deteriorates. In this case, the dispersibility loss can be compensated for by adding a surfactant, although the adhesive strength & water resistance deteriorate in a case where the quantitative ratio of the surfactant is excessively high. Conversely, in a case where the $(A)/(C)$ value is lower than 100/5,000 or where $(C)/(D)$ value exceeds 100/50, the quantitative ratio of the water-soluble organic compound within the aqueous dispersion increases, due to which the persistence of a residual solvent after coating becomes imminent. Cost appreciation, furthermore, becomes unavoidable, and the recovery of said compound must also be taken into consideration. In a case where the $(C)/(D)$ value is lower than 100/10,000, the surface tension of the aqueous dispersion becomes elevated, as a result of which the film wetness diminishes, and coating dots are likely to arise. In this case, the wettability can be enhanced by adding a surfactant, although in a case where the quantitative ratio of the surfactant is excessively high, the adhesive strength & water resistance deteriorate, as in the aforementioned case.

Moreover, zirconium compounds added to this dispersion are instantiated by zirconium ammonium carbonate, zirconium acetate, zirconium nitrate, zirconium sulfate, acidic zirconium /4 chloride [sic: Presumably "zirconium hydrochloride?"], sodium silicozirconate, zirconium oxide, zirconyl stearate, zirconyl octylate, etc., although these examples are not binding. Moreover, zirconium-type polymers are also permissible.

As far as the utilization ratio of (B) with respect to (A) is concerned, it is desirable to satisfy $(A)/(B) = 100,000/5 \sim 100,000/50,000$, preferably $(A)/(B) = 1,000/2 \sim 1,000/200$.

Apart from the hydrolyzate of an alkyl silicate, it is possible to mix, with the polyester copolymer aqueous dispersion thus obtained, such additives as inorganic or organic cross-linking agents, inert particles, lubricants, coloring agents, antistatic agents, electroconductivizing agents, surfactants, defoaming agents, etc. Moreover, it is also possible to mix polymers of the acrylic type, urethane type, epoxy type, polyamide type, rubber type, cellulose type, vinyl ester type, etc.

In a case where the aqueous dispersion of the polyester copolymer thus obtained is coated on a polyester film based on a coating method, said polyester film may be a melt-extruded & yet-to-be-stretched film, a monoaxially stretched film, or a biaxially stretched film, although it is difficult to coat the biaxially stretched film homogeneously in that the film width has become enlarged and that the film traveling speed has become elevated, and therefore, the first two types are more desirable in consideration of the coating agent contiguity, etc.

The coating rate of the aqueous dispersion coated on the polyester film based on the coating method is confined to a range of $0.01 \sim 5.0 \text{ g/m}^2$ in terms of the quantitative ratio of the polyester copolymer existing on the biaxially stretched film. In a case where this coating rate is lower than 0.01 g/m^2 , the force for fixing & binding the zirconium compound becomes attenuated, due to which the lasting performances become aggravated. Conversely, in a case where the coating rate exceeds 5.0 g/m^2 , the slipperiness deteriorates.

In a case where the polyester film is subjected to a corona discharge treatment prior to the coating of the aforementioned polyester copolymer aqueous dispersion, it becomes possible to facilitate the coating of the aqueous dispersion and to improve the adhesive strength in-between the polyester film & polyester copolymer coating film.

In a case where the coated or biaxially stretched polyester copolymer layer is subjected to a corona discharge treatment or, under the pervasion of a nitrogen atmosphere, to a corona discharge treatment or ultraviolet irradiation treatment, it becomes possible to improve the wettability & adhesive strength of the film surface.

In a case where a polyester film, above all a polyethylene terephthalate film, is used as the thermoplastic resin film of the present invention, it is desirable in that the film debris generated in the course of laminating & film preparation processes, etc. can be recovered & reused.

It is desirable, furthermore, for the lubricant content of the polyester to be as low as possible in consideration of flatness, and a level of 300 ppm or below is desirable. A level of 300 ppm or higher may, however, be designated for achieving an advanced lubricancy.

The coated polyester film manufactured by the aforementioned method can be used as a magnetic tape base film, label staker [sic: Presumably “sticker?”] base film, chemical mat base film, overhead projector film, food wrapping film, and all other purposes for which polyester films have been used.

(Application examples)

In the following, application examples of the present invention will be explained. In these application examples, “parts” & “%” are both weight-based figures.

The measurement methods adopted in the application examples are shown below.

(1): Frictional coefficient

Combined measurement values on laminated & non-laminated planes ascertained by using Tensilon (manufactured by Toyo Boseki Co.) in compliance with ASTM-1894.

(2): Film surface flatness

The center line average roughness {RA (μm)} measured by using a Surfcom 300A surface roughness analyzer (manufactured by Tokyo Seimitsu Co.) under the following conditions: Needle diameter: 1 μm ; load: 0.07 g; standard measurement length: 0.8 mm; cut-off: 0.08 mm.

Application Example 1

(1): Manufacture of polyethylene terephthalate

After 2.2 g of lead hydroxide $\text{PbO} \cdot \text{Pb}(\text{OH})_2$ ($\text{Pb} = 0.95 \times 10^{-2}$ mole) had been solubilized into 200 mL of ethylene glycol, 2.0 g of GeO_2 (1.9×10^{-2} mole) was added to the obtained /5 solution, and after the contents had been refluxed & heated at the boiling point of ethylene glycol, namely 197°C, a transparent solution was obtained in approximately 30 min. Next, polyethylene terephthalate was manufactured by using this solution as a polycondensation catalyst. 620 parts of dimethyl terephthalate and 480 parts of ethylene glycol were, together with zinc acetate $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ provided as a transesterification catalyst, reacted, and after the contents had been further polycondensed at a reduced pressure (10 ~ 0.2 mmHg) over a 2-hour period, a polyester copolymer with an average molecular weight of 18,000 and a softening point of 140°C was obtained. 300 parts of this polyester copolymer and 140 parts of n-butyl Cellosolve were agitated & homogenized within a container at 150 ~ 170°C for approximately 3 hours, as a result of a viscous liquid mixture was obtained. After 560 parts of water had been gradually added to this molten liquid, a homogeneous & pale white aqueous dispersion with a solid content concentration of 30% was obtained approximately 1 hour later. 2.5 wt% (with respect to the aforementioned solid content) of zirconium ammonium carbonate was added to & mixed with the obtained aqueous dispersion in an agitated state where ultrasounds were being concomitantly impressed, and after the obtained mixture had been diluted with 1,500 parts of water & 1,500 parts of ethyl alcohol, a coating solution with a solid content concentration of 9% was obtained.

This solution was left unattended at 40°C over a 48-hour period and then subjected to the next process.

(3): Manufacture of coated film

The polyethylene terephthalate manufactured in (1) was melt-extruded at 280 ~ 300°C and then cooled with a 15°C cooling roll, as a result of which a yet-to-be-stretched film with a thickness

of 1,000 μ was obtained, whereas this yet-to-be-stretched film was stretched along the lengthwise direction at a draw ratio of 3.5 by using a pair of 85°C rolls with mutually different circumferential velocities, and after it had been coated with the aforementioned coating solution based on the air knife format, the coated film was dried with a 70°C hot air, and after it had been stretched along the widthwise direction at a draw ratio of 3.5 by using a 98°C tenter, it was thermally fixed at 200 ~ 210°C, as a result of which a biaxially stretched coated polyester film with a thickness of 100 μ was obtained.

The physical properties of the obtained film are shown in Table I. As can be inferred from Table I, the obtained film was flat and excellent in terms of lubricancy.

Application Example 2

A film was obtained according to procedures similar to those in Application Example 1 except that the zirconium ammonium carbonate used in Application Example 1 was substituted with zirconium acetate.

The physical properties of the obtained film are shown in Table I. As can be inferred from Table I, the obtained film was flat was excellent in terms of lubricancy.

Comparative Example 1

A film was obtained according to procedures similar to those in Application Example 1 except that the zirconium ammonium carbonate used in Application Example 1 was dispensed with.

The physical properties of the obtained film are shown in Table I. As can be inferred from Table I, the obtained film was flat, although it was inferior in terms of lubricancy.

Comparative Example 2

A film was obtained according to procedures similar to those in Application Example 1 except that the coating treatment of Application Example 1 was dispensed with.

The physical properties of the obtained film are shown in Table I. As can be inferred from Table I, the obtained film was flat, although it was inferior in terms of lubricancy.

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Table I

	Frictional coefficient		Surface roughness, Ra
	μ_s	μ_d	
Application Example 1	0.42	0.40	0.005
Application Example 2	0.45	0.41	0.005
Comparative Example 1	2.0 <	2.0 <	0.004
Comparative Example 2	2.0 <	2.0 <	0.003

(Effects of the invention)

Thus, the thermoplastic resin film laminate obtained by the method of the present invention is flat and bears a favorable lubricancy.

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